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for project entitled

**INTERNATIONAL COLLABORATION PROGRAM ON INNOVATIVE
CHEMICAL PROCESSING OF SUPERIOR ELECTRONIC
AND OPTICAL MATERIALS**

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ABSTRACT

An international collaborative research project to investigate the preparation and properties of quantum dot materials based on CdS microcrystals in various matrices has been carried out from July 1991 to May 1994. The team consisted of Professor J.D. Mackenzie (P.I.), Professor M. Yamane of the Tokyo Institute of Technology, and Professor N. Peyghambarian of the University of Arizona. Samples were prepared by the Sol-Gel method with sodium borosilicate glass and Ormosils (organically modified silicates) as the matrices. The samples showed no photodarkening effects and have $\chi^{(3)}$ values up to 10^{-6} cgs units. Techniques were developed to limit the size distribution of the CdS while maintaining high concentrations ($> 10\%$). Waveguides were fabricated by the ion-exchange method. At their present developmental stages, the samples suggested the possibility that they can be made into a new type of lasers and also offer the potentials of achieving photochemical hole-burning at room temperature.

1. Introduction

The first phase of the present project was first initiated in October 1, 1987 and concluded on September 30, 1990. The original objective was to utilize a small team of international experts, to pool their knowledge and expertise, and thus to make it more efficient for the development of some superior electronic and optical materials. In particular, chemical processing of two families of relatively new materials was targeted for this collaborative program. These materials were (a) the superconducting ceramics and (b) the nonlinear optical nanocomposites. The original international team consisted of Professor J. Livage of the University of Paris, France, Professor A. Wright of Reading University, U.K., and Professor M. Yamane of the Tokyo Institute of Technology, Japan. Professor Livage would study the chemical reactions of sol-gel based liquid solutions for ceramic superconductors. Professor Wright would study the structures of amorphous gels. Professor Mackenzie would study the preparation of the superconducting ceramics from sol-gel solutions. Professor Yamane would collaborate with Professor Mackenzie on the preparation of quantum dot materials based on the suspension of ultrafine crystals of semiconductors in glassy matrices. Although the program had started in 1987, the collaborative work between Professors Yamane and Mackenzie only began in 1989. This first phase was successfully completed by September 30, 1990. A renewal proposal was submitted in 1990 for the continuation of this project. However, a long delay was experienced in the approval process. It was not until July, 1991 before formal approval was granted and the originally proposed research was severely cut back.

This second phase of the program officially commenced on July 15, 1991. The proposed research on ceramic superconductor was deleted. The research activities of this phase have been concerned only with nonlinear optical materials. The only foreign collaborator has been Professor M. Yamane of the Tokyo Institute of Technology. During the first year, from July 15, 1991 to May 14, 1992, Professor Yamane's support was in the form of travel funds between Japan and Los Angeles, plus living expense for three weeks in Los Angeles where he came to UCLA for discussions. In the second year, the funding was expanded to permit one of professor Yamane's assistants, a Dr. T. Takada, to spend one year at UCLA and one of our Ph.D. students, Ms. Lisa Kao to work at the Tokyo Institute of Technology. In addition, our collaboration

with Professor N. Peyghambarian of the Optical Sciences Center, University of Arizona, has also been increased.

In the final year ending May 14, 1994, Dr. T. Hayashi from Professor Yamane's laboratory replaced Dr. Takada and spent one year at UCLA. We continued to collaborate actively with Professor Peyghambarian of Arizona. This final technical report is a summary of the research performed from July 1991 to May 1994.

2. Research on Semiconductor Quantum Dot Materials based on CdS

Semiconductor quantum dot materials hold promise for a number of important future applications. These include:

- (a) High speed photonic switches with times of 10^{-15} sec versus the fastest electronic switches of about 10^{-12} sec.
- (b) Optical soliton propagation which would minimize dispersion to enable significant improvements in long distance telephone communications.
- (c) High density optical data storage by photochemical Hole-Burning (PHB) at room temperature instead of at extremely low temperatures and at the same time increase storage capacity.
- (d) New semiconductor quantum dot lasers for visible light.

The objectives of our research are:

- (i) To fabricate the best CdS quantum dot samples possible for various applications.
- (ii) To provide the University of Arizona with these samples for device fabrication and testing.
- (iii) To continuously seek improved processes and materials to fabricate quantum dot materials with superior performance and at reduced costs.

2.1 Background

Commercially available filter glasses containing $\text{CdS}_x\text{Se}_{1-x}$ semiconductor quantum dots exhibit large third-order optical nonlinearities. Since the results on nonlinear optical properties of these filter glasses by Jain and Lind in 1983,⁽¹⁾ research on the fabrication and optical properties of quantum dot nanocomposites have been increasing dramatically. However, current quantum dot nanocomposites are not satisfactory for actual device application. In addition, optical properties have been found to strongly depend on origin, i.e., preparation methods of the quantum dot nanocomposites.

Both liquid and solid state hosts have been used to contain semiconductor quantum dots. Because colloids in solution tend to agglomerate and precipitate out of solution, various methods exist to stabilize the colloids and prevent their agglomeration. The synthesis and stabilization of colloidal semiconductor nanoclusters have been reviewed by Steigerwald and Brus.⁽²⁾

Polymer host offers good environment to disperse and stabilize quantum dots.^(3,4) Organic polymers have been proven to be an excellent media for controlling the diffusion of reactants. However, high thermal stability under high energy laser field is still a challenge for organic materials to overcome.

Inorganic crystalline materials have also been used as a matrices for quantum dots. Transparent CdS-doped alumina film has been fabricated by the sol-gel method. The structured environment of zeolite prevents aggregation of clusters due to an open framework of organized pores (3-13Å). Oxide glass matrices provide high transparency with excellent stability to be one of the most promising host materials.

Commercial sharp, cut-off filter glasses, based on silica glass doped with CdS and CdSe microcrystallites, are the first semiconductor quantum dot nanocomposites evaluated for their nonlinear optical response. The colorless, as-cast glass made by glass fusion at high temperatures is subsequently struck at temperatures typically between 700°C and 800°C to cause the formation of microcrystallites in the glass. The position of the sharp absorption edge of these semiconductor quantum dots can be shifted by changing composition and/or microcrystallite sizes through various heat-treatments. However, particle size, size distribution, and composition can vary from one batch to another and from one manufacturer to another. Thus, in early research reports, there were debates on whether the blue shift arises from quantum confinement or from

compositional changes. Furthermore, compositional changes may cause different nonlinear behaviors. For sample, filter glasses made by Schott is more susceptible to photodarkening than those made by Corning.

Unlike glass fusion, the low temperature sol-gel method allows the fine-tuning of material properties through wet chemical route. In sol-gel, liquid reagents are intimately mixed, a solid gel forms upon gelation, and syneresis and the removal of solvents and water occur. The resulting transparent gel has been proven to be a good matrix for colloidal quantum dots. Colloids of HgSe, PbS, In_2Se_3 , CdSe, CdS, Bi_2S_3 , and AgI have successfully been incorporated into silica gel.^(5,6) More recently, experimental results have shown that higher quantum dot concentration and improved particle size control can be achieved by the sol-gel process. However, sol-gel-derived oxide matrices are usually problematic due to inherent brittleness and porosity. Nevertheless, we have developed several types of gel-derived matrices that overcame the later problems.

2.2 Research Accomplishments

Cadmium sulfide quantum dots have been synthesized in three types of matrices from the sol-gel process: pore-free sodium borosilicate (NBS) glass, organically-modified silicates (ORMOSIL), and SiO_2 gel. The first two types were selected as the more promising candidates. The processes are summarized in Figure 1. During the first year we have made the following accomplishments:

- ★ First-generation CdS quantum dots in dense sodium borosilicate glasses were made.
- ★ First-generation CdS quantum dots in dense Ormosils were made.
- ★ Quantum confinement effect was demonstrated.
- ★ High $\chi^{(3)}$ values were obtained from measurements done at the University of Arizona.
- ★ Photodarkening was significantly reduced in sol-gel-derived samples compared to conventional melt-quench-derived sample.

The most significant of these was the minimization of photodarkening. The photodarkening effect has been seen in many samples of microcrystallites in glasses prepared by the melt-quenching technique. We have succeeded in reducing substantially the photodarkening effect in both sol-gel derived NBS and Ormosil matrices. Figure 2 shows that the nonlinear spectra do not change much after extensive exposure to a pump laser with 5 $\mu\text{J}/\text{pulse}$ energy tuned to 451 and 436 nm for the NBS and Ormosil samples, respectively. This is in contrast to the nonlinear spectra for the melt-quench-derived sample which shows a reduction in $-\Delta\alpha L$ by factor of ~ 20 as a result of photodarkening after similar pump exposure conditions. The difference in the photodarkening behavior of these samples is attributed to the different media surrounding the quantum dots. Due to lower silica content, the melt-quenched sample should have more defects compared to the other two; higher content of glass modifiers can provide more sites (defects) for trapping carriers generated by laser light in the semiconductor quantum dots, leading to a much stronger photodarkening effect. Sol-gel samples with higher silica content would be more resistant to photodarkening. Based on similar reasoning for the reduction in photodarkening in sol-gel-derived samples, the luminescence efficiency is also larger in the sol-gel samples, making them suitable for applications in optical storage and lasers.

Some properties obtained on these types of materials are shown in Table 1. Although the results obtained in the first year were satisfactory, it was felt that better control of size distribution of the CdS and confining the sizes in the range of 30 to 40 \AA would lead to better property. Thus, a new technique was developed to narrow the size distribution. This involved the use of a chelating agent, 3-aminopropyl-triethoxysilane (APTES) to anchor the Cd ions to the oxide gel matrix. This new technique is shown in Figure 3. Some TEM results comparing the methods with and without the APTES treatment are shown in Figure 4.

During the second and third years, samples were prepared and sent to the University of Arizona for evaluation as potential devices. In order to realize novel devices, waveguide structures containing quantum dots were fabricated. Recent developments in ion-exchange waveguide fabrication process in glass make it possible to build quantum dot slab and channel waveguide devices. We have succeeded in fabricating channel waveguides in CdS quantum dots in NBS glass samples by the sol-gel technique.

The channel waveguide shown in Figure 5 was made by ion exchange on 15% CdS-doped $5\text{Na}_2\text{O}-15\text{B}_2\text{O}_3-80\text{SiO}_2$ (wt.%) glass. Waveguides of 8 mm in length were fabricated by K^+-Na^+ ion exchange through 5 μm openings. The inset is the near-field mode profile of a waveguide made using a 5 mm-wide mask opening, showing clearly the propagation of single mode light along the waveguide.

Spectral transmission of the CdS quantum dot waveguide shows that the cut-off frequency of the waveguide is near 700 nm, as shown by the drop in transmission. The noise comes mainly from the spectral response of the silicon detector used. The inset is the absorption spectrum of the CdS quantum dot sample itself. The lowest quantum confined transition appears as a shoulder in the spectrum at 420 nm in contrast to bulk CdS bandgap at 512 nm. Optical measurements suggest a high probability of the ability to prepare new lasers using CdS quantum dot materials made by the sol-gel method. In Figure 6, the optical gain achieved is shown.

The dotted curve shows the linear absorption spectrum of the CdS quantum dot itself. The solid curve shows the absorption spectrum when the pump at $\lambda = 560$ nm is present. The pump beam creates carriers that change the absorption spectrum. A large region of gain (negative absorption) is seen. The gain extends from 650 nm to 572 nm. The gain in the region from 620 to 650 nm occurs where no absorption is present. This gain is associated with the "biexciton gain."

There is also some strong indication that these materials can offer spectral hole-burning at room temperature as demonstrated in Figure 7. Room-temperature linear absorption spectrum of the quantum dot material, and its differential absorption spectra after pumping are shown. Two wavelengths were used: 420 (dotted) and 440 nm (solid). The inset shows the change in absorption ($-\Delta\alpha L$) obtained as a result of this pumping. The absorption bleaches and spectral holes are generated which shifts as the pump wavelength is changed.

In general, the second generation samples are much superior to the early samples which were not treated with APTES. Optical measurements at the University of Arizona indicate that the nonlinearity is larger by a factor of 6 as compared to the first generation samples. Even so, there is still room for improvement. At present, we are evaluating various possibilities of

densification at lower temperatures to further minimize size distribution of the CdS.

3. Publications and Presentations

A. Publications

1. Mackenzie, J.D., Li, C.Y. and Xu, Y., "Glasses as Nonlinear Optical Materials," Proc. Int. Conf. Sci. and Tech. **New Glasses**, Japanese Ceramics Society, **101** (1991) 1-10.
2. Mackenzie, J.D., Li, C.Y., Xu, Y., "Glasses as Nonlinear Optical Materials," Chem. Express (Japan), **6** (1991) 903.
3. Chang, Yasumori, A., and Yamane, "Composition of Precursor Solution for the Preparation of the Glass of $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ System using Sodium Acetate," J. Non-Cryst. Solids, **134** (1991) 32.
4. Takada, T., Yano, T., Yasumori, A., Yamane, M., and Mackenzie, J.D., "Preparation of Quantum Size CdS-Doped $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ Glasses with High Nonlinearity," J. Non-Cryst. Solids, **147/148** (1992) 631.
5. Li, C.Y., Wilson, M., Haegel, N.M., Mackenzie, J.D., Knobbe, E.T., Porter, C., Reeves, R.J., "Preparation of Quantum-Size Semiconductor-Doped Ormosils and their Optical Properties," Mat. Res. Soc. Symp. Proc., **272** (1992) 41.
6. L, C.Y. and Mackenzie, J.D., "CdS-doped Ormosils as Nonlinear Optical Materials," SPIE Proc. **Sol-Gel Optics II**, **1692** (1992) 211.
7. Li, C.Y., Tseng, J.Y., Morita, K., Lechner, C., Hu, Y. and Mackenzie, J.D., "ORMOSILs as Matrices in Inorganic-Organic Nanocomposites for Various Optical Applications," SPIE Proc. **Sol-Gel Optics II**, **1758** (1992) 410.
8. Yamane, M., Takada, T., Mackenzie, J.D., Li, C.Y., "Preparation of Quantum Dots by the Sol-Gel Process, SPIE Proc. **Sol-Gel Optics II**, **1758** (1992) 577.
9. Mackenzie, J.D., "Nonlinear Optical Materials by the Sol-Gel Method," J. Sol-Gel Sci. and Tech., **1** (1993) 7-19.

10. Tseng, J.Y., Li, C.Y., Li, Takada, T., Lechner, C., Mackenzie, J.D., "Optical Properties of Metal-Cluster Doped Ormosil Nanocomposites," **SPIE Proc. Sol-Gel Optics II**, **1758** (1992) 612.
11. Mackenzie, J.D., Ed., **Sol-Gel Optics II**, SPIE (1992).
12. Kang, K., Sandalphon, Hu, Y., Koch, S., Peyghambarian, N., Li, C., Takada, T., Mackenzie, J.D., Liu, L., Risbud, S., "Nonlinear Optical Properties of CdS Quantum Dots prepared by Sol-Gel Technique: Spectral Hole Burning and Photodarkening," in Conference on **Lasers and Electro-Optics**, 1993, Vol. 11, OSA Technical Digest Series (Optical Society of America, Washington, D.C., 1993), pp. 618-620.
13. Wilson, M., Li, C., Mackenzie, J.D. and Haegel, N.M., "Photoluminescence Excitation Spectroscopy Study of CdS Nanocrystals in Ormosils," **Nanostructured Materials**, **2**[4] (1993) 391-398.
14. Kang, K., Kepner, A., Hu, Y., Koch, S., Peyghambarian, N., Li, C., Takada, T., Kao, L. and Mackenzie, J.D., "Room Temperature Spectral Hole-Burning and Elimination of Photodarkening in Sol-Gel Derived CdS Quantum Dots," **Appl. Phys. Lett.**, **64**[12] (1994) 1487-1489.
15. Takada, T., Li, C., Tseng, J., Mackenzie, J.D., "Control of Particle Size Distribution of CdS Quantum Dots in Gel Matrix," **J. Sol-Gel Sci. and Tech.**, **1**(1994) 123-132.
16. Peyghambarian, N., Tajalli, H., Wright, E., Koch, S., Najafi, S., Hulin, D. and Mackenzie, J.D., "Quantum Dot Glass Integrated Optical Devices," in **Glass Integrated Optics and Optical Fiber Devices**, S. Najafi, Ed., SPIE Proc. **CR53** (1994) 211-234.
17. Mackenzie, J.D. and Y. Kao, Y., "Sol-Gel Process for Glass Integrated Optics," in **Glass Integrated Optics and Optical Fiber Devices**, S. Najafi, Ed., SPIE Proc. **CR53** (1994) 83-113.
18. Mackenzie, J.D., and Kao, Y., "CdS Quantum Dot Materials by the Sol Gel Method", in **Nonlinear Optics for High-Speed Electronics and Optical Frequency Conversion**, N. Peyghambarian, Everitt, H., Eckardt, R., and Lowenthal, D., Eds., SPIE Proc. **2145** (1994) 90-101.
19. Kao, Y., Hu, Y., Zheng, H., Mackenzie, J.D., Perry, K., Bounhill, G., and Perry, J., "Second-Harmonic Generation in Transparent Barium Borate Glass-Ceramics," **J. Non-Crys. Solids**, **167**[3] (1994) 247-254.

20. Takada, T., Mackenzie, J.D., Yamane, M., Kang, K., Peyghambarian, N., Reeves, R., Knobbe, E. and Powell, R., "Preparation and Nonlinear Optical Properties of CdS Quantum Dots in Na₂O-B₂O₃-SiO₂ Glasses by the Sol-Gel Process," J. Optical Society of America, B (1994) (submitted).
21. Mackenzie, J.D. and Kao, Y., "Transparent glass nanocomposites and their Nonlinear Optical Properties," Glastech. Berlin (in press).
22. Kao, Y., Hayashi, K., Yu, L., Yamane, M., Mackenzie, J.D., "Preparation of Narrow Size Distribution CdS Quantum Dots in Sodium Borosilicate Glass by the Sol-Gel Process," in **Sol-Gel Optics III**, J. Mackenzie, Ed., SPIE Proc. **2288** (1994) (in press).
23. Li, C., Y. Kao, K. Hayashi, T. Takada, and J. Mackenzie, "Improving CdS Quantum Dot Materials by the Sol-Gel Process," in **Sol-Gel Optics III**, Mackenzie, J.D. Ed., SPIE Proceedings, **2288**, 1994 (in press).
24. Lee, S., Kang, K., Guerreiro, P., Wright, E., Peyghambarian, N., Najafi, S., Zhang, G., Li, C., Takada, T., and Mackenzie, J.D., "Fabrication, Optical Characterization and Femtosecond Pulse Propagation in a Semiconductor Quantum Dot Waveguide," in Conference on **Lasers and Electro-Optics**, 1994 OSA Technical Digest Series (Optical Society of America, Washington, D.C., 1994) (in press).

B. Presentations

1. Peyghambarian, N., Tajalli, H., Wright, E., Koch, S., Najafi, S., Hulin, D. and Mackenzie, J.D., "Quantum Dot Glass Integrated Optical Devices," Paper presented at SPIE Proc. (Critical Review) San Diego, California, July 24-29, 1994.
2. Mackenzie J.D. and Kao, Y., "Sol-Gel Process for Glass Integrated Optics," paper presented at SPIE Proc. (Critical Review) San Diego, California, July 24-29, 1994.
3. J.D. Mackenzie and Y. Kao, "CdS Quantum Dot Materials by the Sol-Gel Method", paper presented at SPIE Proc., Los Angeles, California, January 24-26, 1994.
4. Y. Kao, K. Hayashi, L. Yu, M. Yan and Mackenzie, "Preparation of Narrow Size Distribution CdS Quantum Dots in Sodium Borosilicate Glass by the Sol-Gel Process," paper presented at SPIE Proc. San Diego, California, July 24-29, 1994.

5. Li, C., Kao, Y., Hayashi, K., Takada, T., and Mackenzie, J.D., "Improving CdS Quantum Dot Materials by the Sol-Gel Process," paper presented at SPIE Proc. **Sol-Gel Optics III**, San Diego, California, July 24-29, 1994.
6. Lee, S., Kang, K., Guerreiro, P., Wright, E., Peyghambarian, N., Najafi, S., Zhang, G., Li, C., Takada, T., and Mackenzie, J.D., "Fabrication, Optical Characterization and Femtosecond Pulse Propagation in a Semiconductor Quantum Dot Waveguide," paper presented at Conference on **Lasers and Electro-Optics**, Anaheim, California, 1994.
7. Mackenzie, J.D. and Kao, Y., "Transparent Glass Nanocomposites and their Nonlinear Optical Properties," paper presented at **Fifth International Otto Schott Colloquium**, Jena, Germany, July 10-14, 1994.
8. Li, C., Wilson, M., Haegel, N., Mackenzie, J.D., Knobbe, E., Porter, C., Reeves, R., "Preparation of Quantum-Size Semiconductor-Doped Ormosils and their Optical Properties," paper presented at Mat. Res. Soc. Symp., San Francisco, California, 1992.
9. Yaane, M., Takada, T., Mackenzie, J.D., Li, C.Y., "Preparation of Quantum Dots by the Sol-Gel Process," SPIE Proc. **Sol-Gel Optics II**, San Diego, CA, July 20-22, 1992.
10. Peyghambarian, N., Tajalli, H., Wright, E., Koch, S., Najafi, S., Hulin, D., and Mackenzie, J.D., "Quantum Dot Glass Integrated Optical Devices," paper presented at SPIE Proc. (Critical Review) **Sol-Gel Optics III**, San Diego, CA, July 24-29, 1994.
11. Mackenzie, J.D., and Kao, Y., "Sol-Gel Process for Glass Integrated Optics," paper presented at SPIE Proc. **Sol-Gel Optics III**, San Diego, CA, July 24-29, 1994.
12. Mackenzie, J.D. and Kao, Y., "CdS Quantum Dot Materials by the Sol-Gel Method," paper presented at SPIE Proc. Los Angeles, CA, January 24-26, 1994.
13. Kao, Y., Hayashi, K., Lu, L., Yamane, M., Mackenzie, J.D., "Preparation of Narrow Size Distribution CdS Quantum Dots in Sodium Borosilicate Glass by the Sol-Gel Process," paper presented at SPIE Proc. **Sol-Gel Optics III**, San Diego, CA, July 24-29, 1994.
14. Li, C., Kao, Y., Hayashi, K., Takada, T., and Mackenzie, J.D., "Improving CdS Quantum Dot Materials by the Sol-Gel Process," paper presented at SPIE Proc. **Sol-Gel Optics III**, San Diego, CA, July 24-29, 1994.

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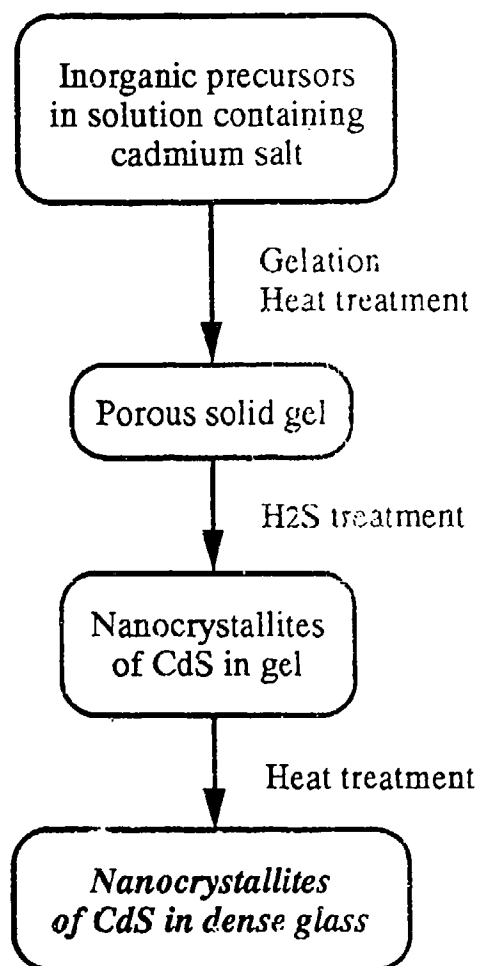
4. Personnel

Professor J.D. Mackenzie has been the Principal Investigator. external collaborators were Professor M. Yamane, Tokyo Institute of Technology, Professor N. Peyghambarian, University of Arizona. Visiting scientists from Professor Yamane's group were Dr. T. Takada (1992-93) and Dr. K. Hayashi (1993-94). C.Y. Li received his Ph.D. degree in 1993 and Justine Tseng received her M.S. also in 1993 from research performed on this grant. Dr. Xu Yuhuan, Research Associate, has been working part-time on this project. Ms. Yu Hua Kao has been doing research for her Ph.D. thesis on this project. Ms. Kao visited the Tokyo Institute of Technology to work with Professor Yamane in 1993.

5. REFERENCES

1. Jain, R.K. and Lind, R.C., J. Optical Society America, **73** (1983) 6647.
2. Steigerwald, M.L. and Brus, L.E., Ann. Rev. Mater. Sci., **19** (1989) 471.
3. Wang, Y. and Mahler, M., Opt. Commun., **61** (1988) 233.
4. Hilinski, E., Lucas, P., and Wang, Y., J. Chem. Phys. **89** (1988) 3435.
5. Rajh, T., Vucemilovic, M.I., Dimitrijevic, N.M., Micic, O.I., Chem. Phys. Lett., **143** (1988) 305.
6. Modes, S. and Lianos, P., Chem. Phys. Lett., **153** (1988) 351.

*Dense Sodium Borosilicate
Glass as Matrix*



*New Organically-Modified
Silicate (Ormosil) as Matrix*

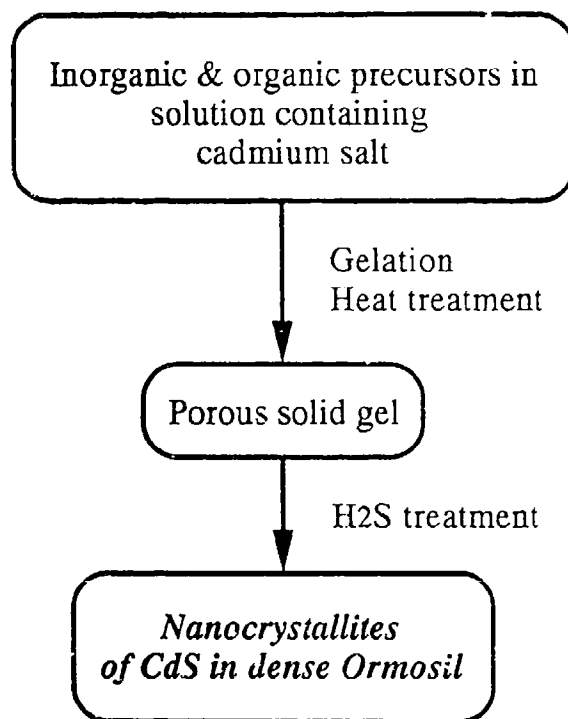


Figure 1 Two types of sol-gel based processes for quantum dot materials

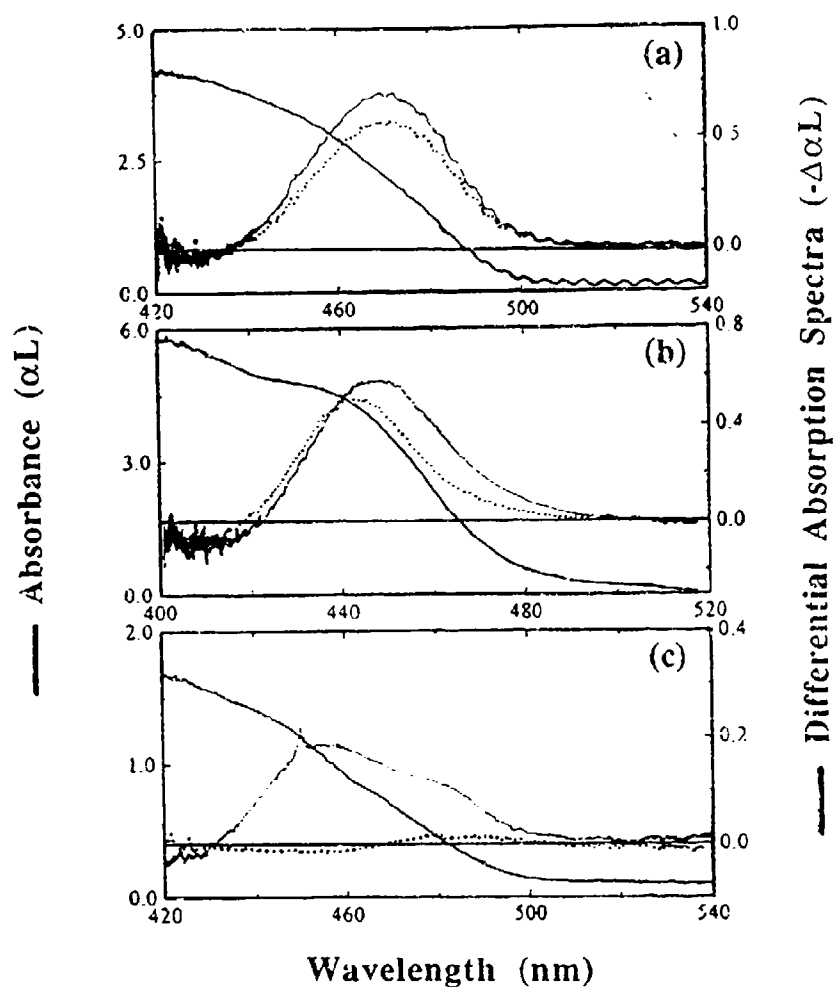


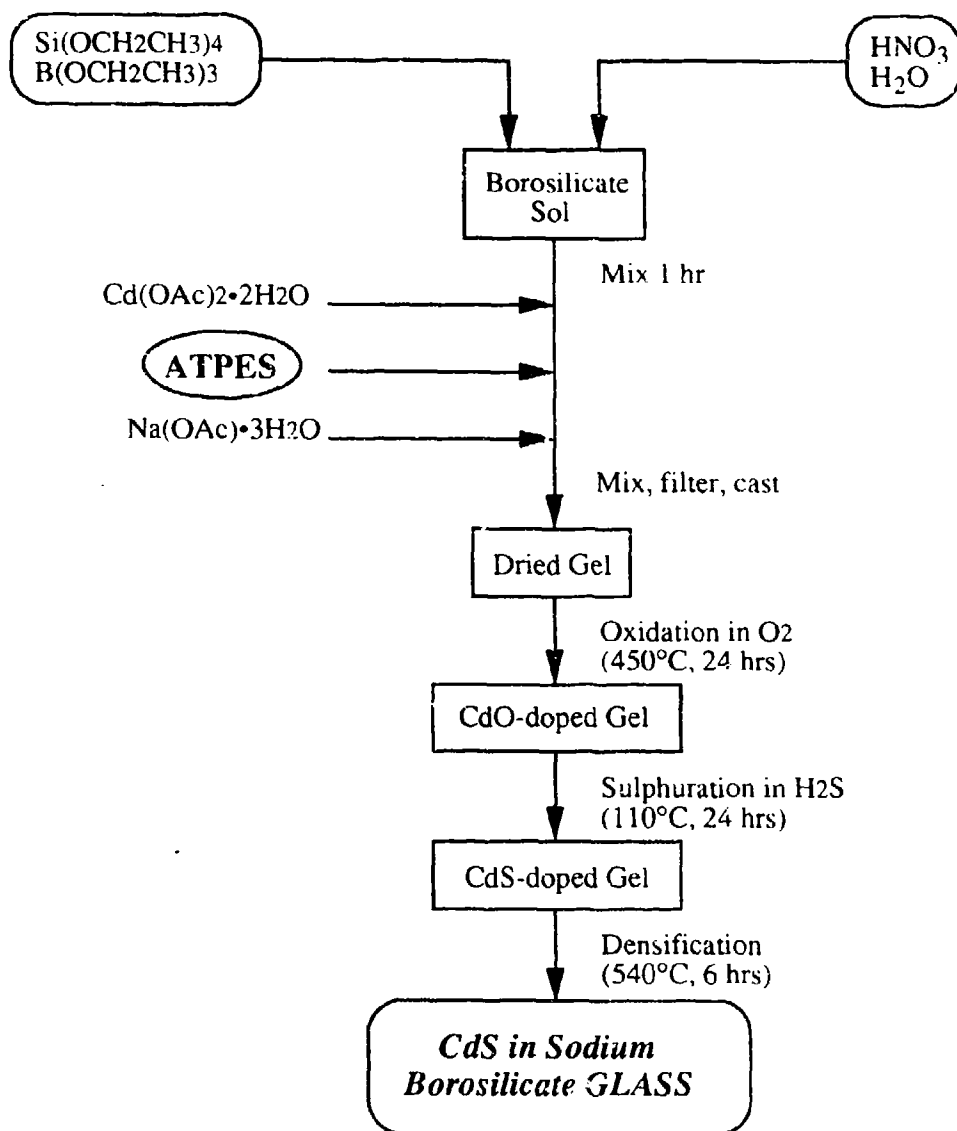
Figure 2 Linear absorption spectra and negative differential absorption spectra of CdS quantum dots in different materials

- (a) Sol-gel-derived sodium borosilicate (NBS) glass [$\lambda_{\text{pump}} = 451 \text{ nm}$]
- (b) Sol-gel-derived organically-modified silicate (Ormosil) [$\lambda_{\text{pump}} = 436 \text{ nm}$]
- (c) Melt-quenched glass [$\lambda_{\text{pump}} = 451 \text{ nm}$]

— Before pump exposure
 After extensive pump exposure.
 Pump intensity = 400 kW/cm^2

Figure 3. PREPARATION OF CdS-DOPED SODIUM BOROSILICATE GLASSES WITH CONTROLLED SIZE DISTRIBUTION

(SECOND GENERATION SAMPLES)



APTES

$\text{NH}_2(\text{CH}_2)_3\text{--Si}(\text{OCH}_2\text{CH}_3)_3$

A bifunctional ligand used to anchor the Cd^{2+} ions to the gel matrix for improved particle size control.

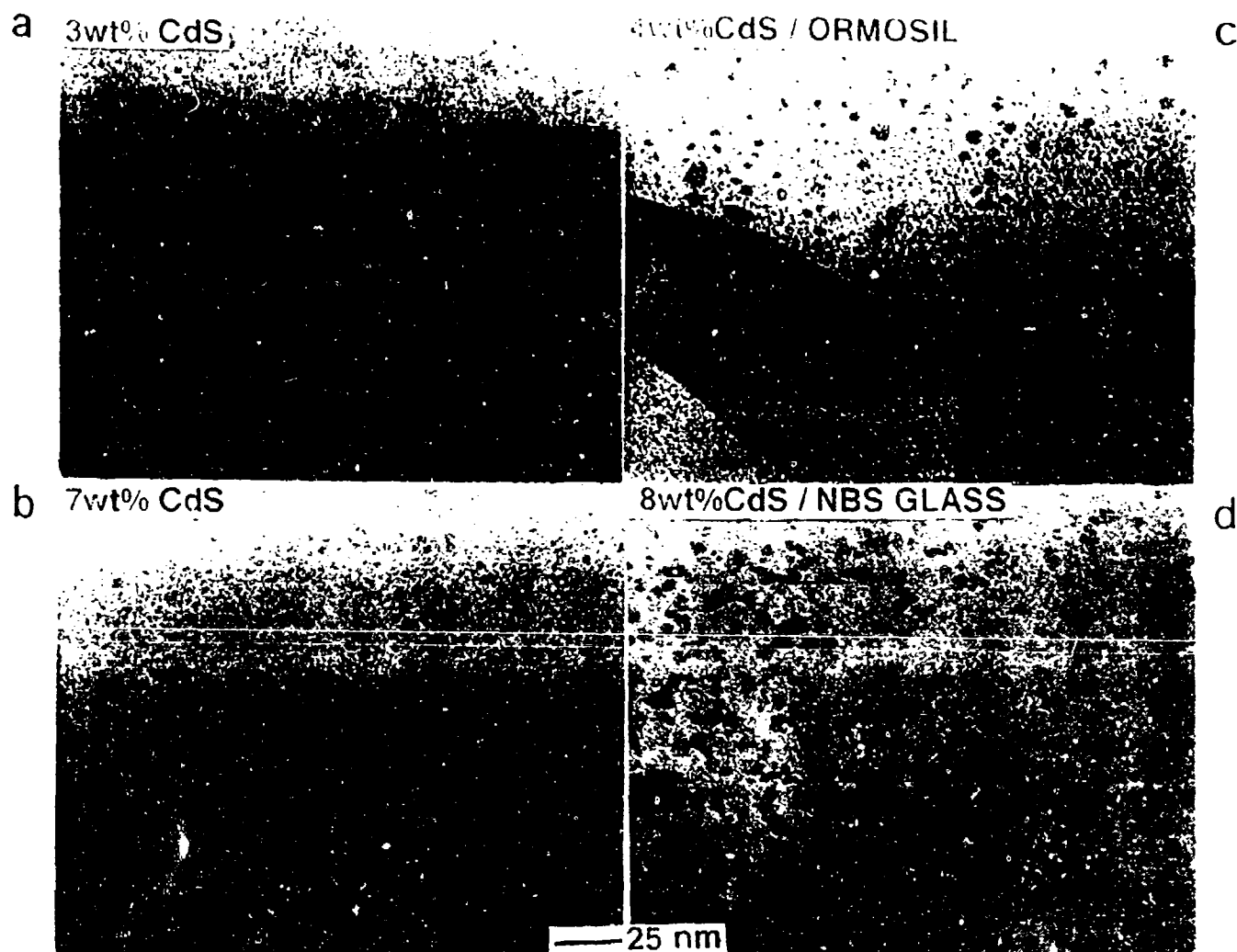
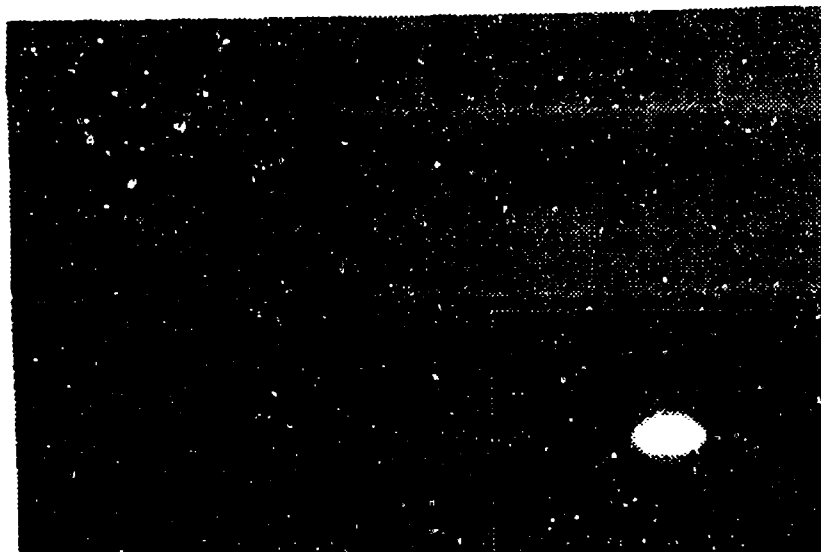
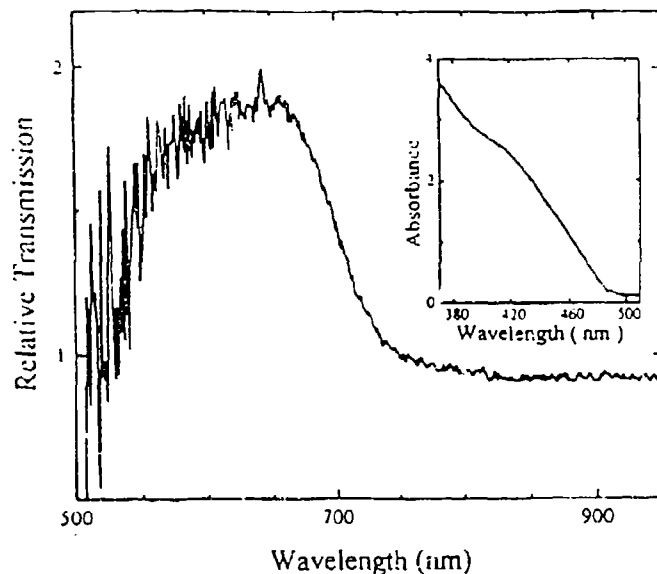


Figure 4 Transmission electron micrographs of CdS quantum dot materials made by the sol-gel process

- (a) 3 wt.% CdS in APTES-modified SiO_2 gel matrix
- (b) 7 wt.% CdS in APTES-modified SiO_2 matrix
- (c) 4 wt.% CdS in Ormosil (TEOS-PDMS) matrix without APTES
- (d) 8 wt.% CdS in $5\text{Na}_2\text{O}-15\text{B}_2\text{O}_3-80\text{SiO}_2$ (wt.%) glass without APTES



Microscope photograph of potassium ion-exchanged CdS quantum dot glass channel waveguide. Inset is the near-field mode profile of a waveguide made using a 5 μm -wide mask opening, showing clearly the propagation of single mode light along the waveguide.



Spectral transmission of the CdS quantum dot waveguide. The cut-off frequency of the waveguide is near 700 nm, as shown by the drop in transmission. The inset is the absorption spectrum of the CdS quantum dot material itself.

Figure 5

Figure 6 Optical gain in CdS quantum dot-doped glasses made by the sol-gel method

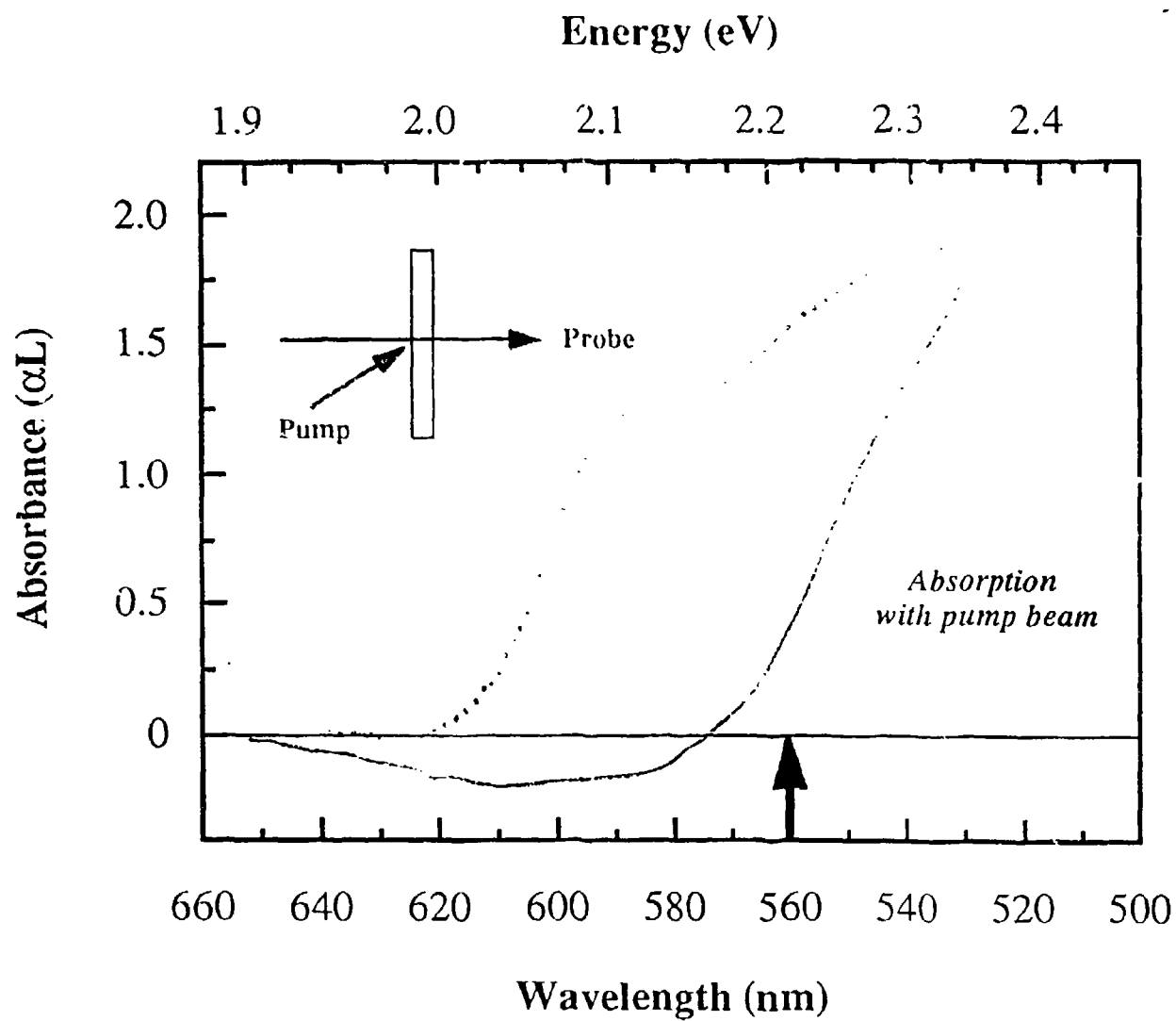


Figure 7 Room-Temperature Spectral Hole-Burning in CdS Quantum Dot-Doped Glasses made by the Sol-Gel Method

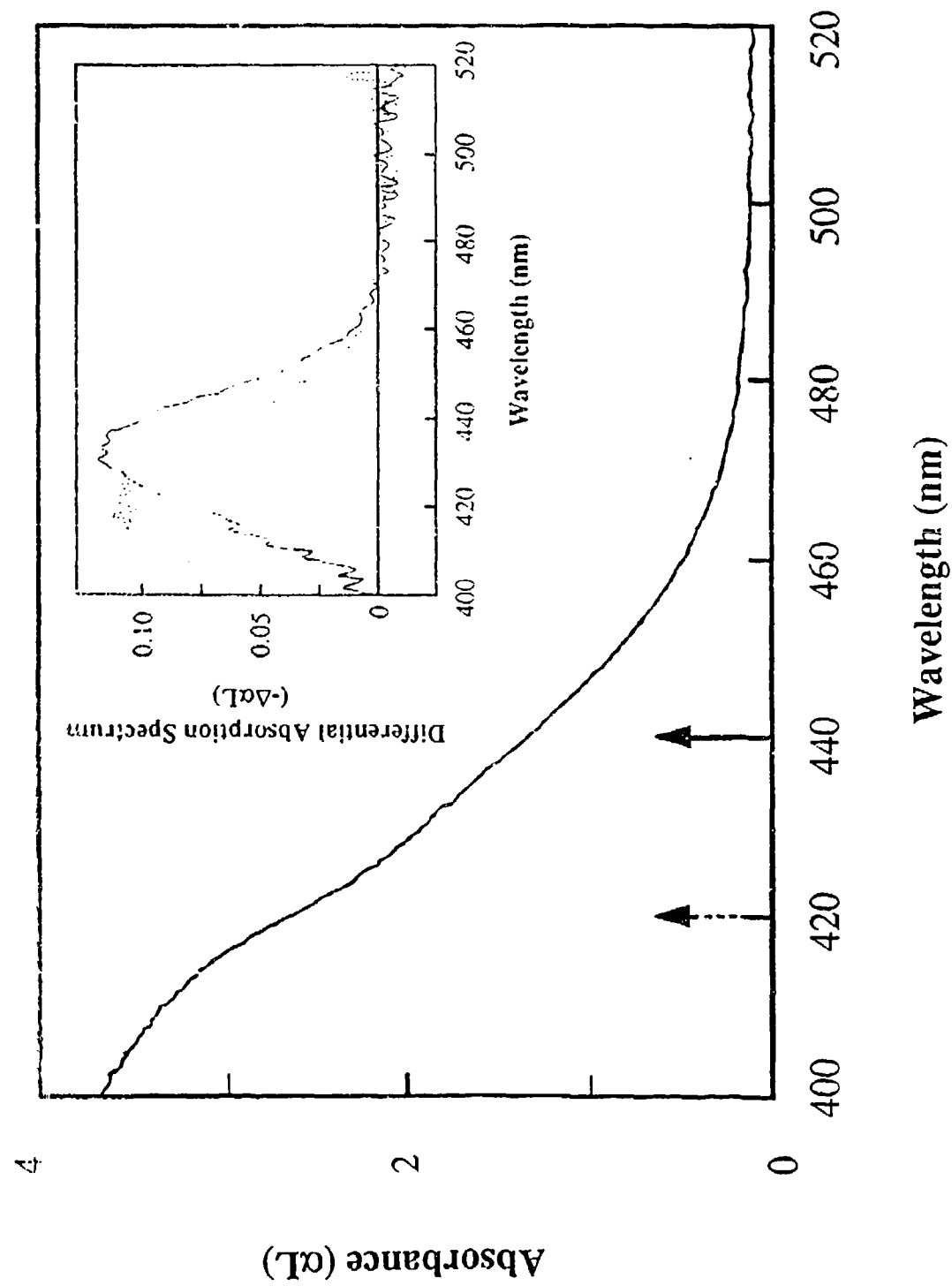


Table 1

**Unique Properties of CdS Quantum Dot Materials made by the
Sol-Ge! Process**

<i>Property</i>	<i>Sodium Borosilicate Matrix</i>	<i>Ormocil Matrix</i>
Maximum CdS content (wt.%)	11	20
CdS quantum dot size (nm)	3 to 7	2 to 7
Nonlinearity, $\chi^{(3)}$ On-resonant (esu) Off-resonant (esu)	10^{-6} to 10^{-7} 10^{-11} to 10^{-12}	10^{-7} to 10^{-8} 10^{-11} to 10^{-13}
Photodarkening	Resistant	Resistant
Matrix microstructure	Pore-free glass	Gel
Mechanical properties	Similar to glass (polishable to 15 μm)	Vickers hardness number of 160
Waveguide fabrication	Ion exchange (bulk glass)	Sol-gel coating (crack-free film)